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A METHOD OF REMOVING INK FROM USED PAPER

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A METHOD OF REMOVING INK FROM USED PAPER

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[There are no amendments to this patent.]

### Claim

A method of removing ink from used paper, characterized by the use of alkali-resistant cellulase in the process of removing ink by treating used paper with ink-removal chemicals.

### Detailed explanation of the invention

#### Industrial application field

The present invention concerns a method of removing ink by treating used paper by ink-removal chemicals.

#### Conventional technology

Various methods of removing ink by treating used paper with ink-removal chemicals are known.

In order to remove ink from used paper and regenerate pulp, decompose old paper by a pulper or some other device and treat it with the addition of alkali substances such as NaOH,  $\text{Na}_2\text{Cl}_3$ , and silicic acid soda, oxidizing agents such as surface-active agents and hydrogen peroxide, and bleaching agents. To this, add pH stabilizers, chelating agents, and dispersants for treatment as additional agents. This will accelerate the separation of the printing ink from the pulp resin. Separate the pulp and ink by such processes as flotation and washing. Generally, the resin part alone is used as regenerated pulp for the production of paper.

## Problems to be solved by the invention

Recently, more and more of such resins as petroleum resins and phenol resins are being consumed as a vehicle for printing ink because of the demand for more beautiful and fast printing materials and a demand for an improvement of the printing task capability. These resins make it more difficult to remove ink from collected used paper. When such used paper was treated by a previous ink-removal method, the regenerated pulp had ink specks in it and presented a problem of poor appearance of the paper.

For this reason, as a method of treating used paper that was resistant to the removal of ink, many methods were tried and disclosed. They include increasing the basicity of NaOH,  $\text{Na}_2\text{CO}_3$ , silicic acid soda, etc., performing a treatment at a high pulp concentration, prolonging the time for ink removal, and separating the ink from the pulp resin by making the ink particles very small through chemical dispersion by a kneader or a disperser.

The purpose of the present invention is to offer a method of removing ink from used paper, in which cellulase, an enzyme used for the hydrolysis of cellulose, is unconventionally used to soften the ink strongly attached to the pulp resin by causing a mild hydrolysis on the surface of the resin, accelerating the separation of the ink.

## Means to solve the problems

The present invention concerns a method of removing ink from used paper, characterized by the use of alkali-resistant

cellulase in the process of removing ink by treating used paper by ink-removal chemicals.

Cellulase is known as an enzyme for the hydrolysis of cellulose. So far, it has been used as an accelerator in the cooking of lignocellulose products such as wood and in the beating of pulp. Yet, cellulase was never used in the ink removal of used paper.

Ordinarily, cellulase is reactive under an acidic to neutral pH (best at pH 4-5). It loses its reactivity under basic conditions of pH 8 or more.

The ink-removal reaction proceeds under basic conditions. Thus, if we do not use an alkali resistant cellulase which has enzyme activity on the basic side, we cannot expect a better effect than the previous ink-removal methods.

Ordinary cellulase is obtained from Trichoderma viride, Aspergillus niger, etc., but these all lose their reactivities under basic conditions.

The present inventors, after many trials, confirmed that an alkali-resistant cellulase could be obtained from Humicola insolens and that this would achieve the above objective by being placed in the ink-removal process. Thus, the present invention was completed.

Use this alkali-resistant cellulase at 0.01-1% of the used paper weight (of bone-dry used paper weight), preferably 0.03-0.3%. The reason why we limit the amount of addition to 0.01-1% is that when the amount is less than 0.01%, the effect of ink removal decreases, while when the amount is over 1%, the hydrolysis of the pulp proceeds too far and decreases the strength of the paper.

As for the usage of this alkali resistant cellulase, add this to used paper 30 minutes to one hour after the addition of the usual ink-removal chemicals, or add the alkali-resistant cellulase along with the ink-removal chemicals and leave them at 40-60°C for 1-6 hours. In adding the cellulase, the reason why we add it 30 minutes to one hour after the addition of the ink-removal chemicals is that generally when the concentration of  $H_2O_2$  is too high, cellulase loses its reactivity. Thus, it is necessary to add cellulase when  $H_2O_2$  has already reacted with the used paper and it has been consumed to a lower concentration. However, if you do not use  $H_2O_2$ , or if its amount of use is less than 1%, it is appropriate to add cellulase in less than 30 minutes. Again, after the addition of cellulase, there must be at least one hour for the contact between the ink and the cellulase. When the reaction time exceeds six hours, a better result cannot be expected. This is also not economical since it requires a larger facility. Again, you can independently use the treatment with alkali-resistant cellulase as one step in the ink-removal process. Cellulase can be very well separated by flotation and washing, whether it is added with ink-removal chemicals or it is added separately.

For the used paper in the present invention, you can use any type of so-called used papers, such as mechanical pulp, used newspaper containing chemical pulp, magazine used paper, low to medium-degree printing used paper, high-quality used paper made of chemical pulp, and such printing used paper as coated paper made of these various types.

The ink-removal chemicals mentioned in the invention are those chemicals that are generally used to remove ink from used

paper. Examples include alkali such as NaOH and  $\text{Na}_2\text{CO}_3$ , silicic acid soda, hydrogen peroxide, phosphate, anionic and nonionic surface-active agents, scavengers such as oleic acid, and additional agents such as a pH stabilizer, chelating agent, and dispersant.

As for the ink-removal processes that can be used in the present invention, it is appropriate to use variously improved methods that have been tried in the ink-removal process in the past, in addition to the already well-known ink-removal processes.

#### Application example

Application examples of the present invention are presented in the following.

#### Application Example 1

Cut used newspaper by 3 cm x 3 cm and add 75 g of this to a 3-L elution device. Stir the material for 3 minutes at a 5% concentration. To this, add NaOH at 1%,  $\text{H}_2\text{O}_2$  at 1%, silicic acid soda at 3%, and a nonionic surface-active agent at 0.2% and allow the mixture to react for 20 minutes at 50°C. Next, add to the above an alkali-resistant cellulase obtained from Humicola insolens (Cellulase SP227 produced by the Nopo Co.) by 0.1% (all of the above amounts of addition are % of bone-dry used paper weight; the same is true below) and allow the mixture to react for two hours. Dilute this to a 1% concentration and carry out flotation for 10 minutes by a testing flotation device (Denver

type). After the reaction is completed obtain 100 g/m<sup>2</sup> of handmade paper by maintaining the pH as is (pH 9.1), then by decreasing the pH to 5.0 according to the band, and measure the degree of whiteness of the paper. For comparison, produce other handmade paper in exactly the same manner as is Application Example 1 except do not add alkali-resistant cellulase, then measure the degree of whiteness. The results are shown in Table I.

Table I.

| 1   | 2 pH     | 3 实施例 1 | 4 比較例 1 |
|-----|----------|---------|---------|
| 白色度 | そのまま 5   | 58.5    | 54.9    |
|     | 5.0に調整 6 | 57.0    | 52.1    |

7 試験法、白色度 JIS P-8123

- Key: 1. Degree of white color  
 2. pH  
 3. Application Example 1  
 4. Comparative Example 1  
 5. Maintain the present pH  
 6. Decreased to 5.0  
 7. Testing method, degree of whiteness JIS P-8123

### Application Example 2

Cut used simili [transliteration] by 3 cm x 3 cm, place 75 g of this paper into a 3-L elution device and stir the material for 5 minutes at a 5% concentration. To this, add NaOH at 1%, a nonionic surface-active agent at 0.1%, and alkali-resistant cellulase (same as that used in Application Example 1) at 0.05% and allow the mixture to react for three hours at 50°C. Next,



dilute the above product to a 1% concentration and carry out flotation for 10 minutes using a testing flotation device.

Wash the product with an 80-mesh standard screen and to this add hypochlorous acid soda by 1% of pulp. Bleach the material for three hours at 40°C. After bleaching is completed, obtain 100 g/m<sup>2</sup> of handmade paper and measure the degree of whiteness.

For comparison, perform another ink-removal reaction in the same manner as in Application Example 2 except for not adding alkali resistant cellulase. The results are shown in Table II.

Table II.

|                                    | 3 例 2 | 2 比較例 2 |
|------------------------------------|-------|---------|
| 3 白色度                              | 80.3  | 78.9    |
| 4 残インキ量<br>(mm <sup>2</sup> /100g) | 15    | 39      |

5 試験法: 残インキ量

- Key: 1. Application Example 2  
 2. Comparative Example 2  
 3. Degree of whiteness  
 4. Resin of remaining ink  
 5. Testing method: resin of remaining ink

Measure the resin area of the surface of the handmade paper to which the ink still remains, based on the JIS P-8208 pulp foreign-matter test.

### Application Example 3

Cut used newspaper by 3 cm x 3 cm and add 75 g of this to a 3-L elution device and stir the material for three minutes at a

5% concentration. To this, add NaOH at 1%, a nonionic surface-active agent at 0.1%, and alkali-resistant cellulase at 0.5%, respectively, and decompose the paper. After leaving the material for five hours, add H<sub>2</sub>O<sub>2</sub> at 1% and silicic acid soda at 2% and leave the mixture for another hour. Dilute this to a 1% concentration and carry out flotation for 10 minutes using a flotation device and separate the ink from the pulp.

After the separation is completed, maintain the pH as is, then decrease it to 4.5 according to the band. Obtain 100 g/m<sup>2</sup> of handmade paper and measure the degree of whiteness. For comparison, produce more handmade paper in exactly the same manner except for not adding alkali-resistant cellulase and measure the degree of whiteness. The results are shown in Table III.

Table III.

| 1<br>白度 | pH       | 2 又は 例 3 | 3 又は 例 3 |
|---------|----------|----------|----------|
|         | 4.5 のまま  | 59.6     | 52.1     |
|         | 5.5 に 調整 | 57.3     | 49.0     |

- Key: 1. Degree of whiteness  
 2. Application Example 3  
 3. Comparative Example 3  
 4. Maintain the present pH  
 5. Decreased pH to 4.5

According to the application and comparative examples, in removing ink from used newspaper and used simili, as a result of carrying out an ink-removal reaction by adding alkali-resistant cellulase with ink-removal chemicals (Application Examples 2, 3) or by adding the cellulase separately (Application Example 1),

the degree of whiteness of the regenerated pulp became greater than that of the sample without cellulase (Comparative Examples 1-3). Again, when we decreased the pH in the ordinary papermaking conditions to pH 4.5-5.0 by aluminum sulfate (band), almost all of the colloidal coloring materials and fine carbon particles in the pulp suspension solution were deposited onto the resin. Under these conditions, the degree of whiteness obtained by the present invention was greater. This shows that any coloring particles can be efficiently separated and removed from the resin by a cellulase treatment. Again, in Application Example 2, we measured the resin of the remaining ink. The result was less than half of that without cellulase (Comparative Example 2). The results of the application and comparative examples and preliminary tests confirm that, concerning the addition conditions of the alkali-resistant cellulase of the present invention, the amount of addition should be 0.01-1% of the used paper's bone-dry weight, preferably 0.03-0.3%. The above results also confirm that after cellulase is added, the mixture is preferably left to react for 1-6 hours. Again, when you add cellulase separately after the addition of ink-removal chemicals containing  $H_2O_2$ , it is preferred to add cellulase 30 minutes to one hour after the addition of the chemicals. However, when the addition amount of  $H_2O_2$  in the ink-removal chemicals is very small, such as less than 1%, it is appropriate to add cellulase within 30 minutes since the concentration of  $H_2O_2$  is so low that it hardly affects the cellulase.

## Effect of the invention

It was previously considered that cellulase could work only under acidic conditions and that cellulase could not be used for the removal of ink since it loses its reactivity on the basic side. However, the method of removing ink from used paper in the present invention disclosed an alkali-resistant cellulase. Placing this in the ink-removal process with ordinary ink-removal chemicals improved the degree of whiteness of the regenerated pulp after the removal of ink and realized a drastic decrease in the resin of the remaining ink. This alkali-resistant cellulase not only can be used in the ordinary ink-removal processes, but also can be placed in the various improved ink-removal processes as needed. Thus, it is possible to broaden its usage and improve the qualities of used paper pulp in general.